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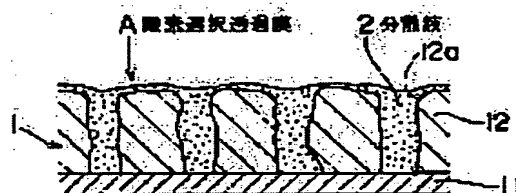
## (54) OXYGEN PERMSELECTIVE FILM AND CELL USING THE FILM

(57)Abstract:

PURPOSE: To obtain an oxygen permselective film capable of preventing going out or in of water vapor and penetration of carbon dioxide by a method wherein a solution of an oxygen transporting carrier enveloping a metallic complex reversely bonded to oxygen is made into a film under a state wherein a dispersion liquid dispersed in an solute which is hydrophobic and slow in dissolving speed of carbon dioxide gels.

CONSTITUTION: In an oxygen permselective film A applied to an air cell or the like equipped with a gas dispersion electrode using oxygen as an active material, the film is made by impregnating a through hole 12a of a porous layer 12 of a porous support film

1 consisting of a basic film 11 and the porous layer 12 with a fluid dispersion 2. Then, after a dispersed oxygen transporting carrier solution adsorbs oxygen selectively in the fluid dispersion 2, oxygen is dispersed in the fluid dispersion 2 to detach or attach oxygen, and oxygen is made to permeate selectively the film. The fluid dispersion 2 is adjusted by dispersing the oxygen transporting carrier solution enveloping a metallic complex unusually reversibly bonded to oxygen into a solution which is hydrophobic and slow in



dissolving speed of carbon dioxide, and a film is made in a gel state by a gelling agent swelled by the solute.

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CLAIMS

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[Claim(s)]

[Claim 1] Oxygen permselective membrane characterized by film-izing the dispersion liquid which it is [ dispersion liquid ] hydrophobicity and distributed the solution of the oxygen transporter containing the metal complex which considers specific and reversible association as oxygen in the medium with the slow dissolution rate of a carbon dioxide.

[Claim 2] Oxygen permselective membrane according to claim 1 which film-ized dispersion liquid in the condition of having gelled with the gelling agent swollen by the medium.

[Claim 3] Oxygen permselective membrane characterized by film-izing the oxygen resolvent which dissolves oxygen alternatively in the state of gel.

[Claim 4] Oxygen permselective membrane according to claim 3 which gelled the oxygen resolvent with absorptivity resin.

[Claim 5] The cell characterized by making oxygen permselective membrane according to claim 1 to 4 intervene between this gas diffusion electrode and an air introduction hole while preparing the gas diffusion electrode which uses oxygen as an active material along with the above-mentioned air introduction hole in the cell container which has the air introduction hole which leads to the open air.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the oxygen permselective membrane which has the function which penetrates oxygen gas alternatively, and cells using it, such as an air cell and a fuel cell.

[0002]

[Description of the Prior Art] Generally in the cell equipped with the gas diffusion electrode which uses oxygen, such as the above-mentioned air cell and a fuel cell, for an active material, using the oxygen in the air which prepared the air introduction hole which leads to the open air, and was adopted from here for a cell container as an active material is performed. Although many properties of the above-mentioned cell, such as internal resistance of a cell and a discharge property, are stable in extent with which practical use is presented, the much more stability and reinforcement are desired and the development to reinforcement is continued.

[0003] for example, fluctuation of the concentration of the electrolytic solution in a cell by a steam going in and out from the introduction hole of air, as for the conventional cell, and the volume -- or there is a possibility by absorption of the carbon dioxide which invaded from the introduction hole of the above-mentioned air that degradation of the electrolytic solution etc. may arise. For example, as a result of this electrolytic solution's incorporating external moisture and producing a concentration fall and cubical expansion if relative humidity is higher than 45 - 59% when the potassium-hydroxide water solution whose concentration is about 30 - 35% is used as the electrolytic solution, there is a possibility may produce discharge performance degradation, the leakage of the electrolytic solution, etc., when relative humidity is conversely lower than the above-mentioned range, evaporation of the electrolytic solution starts and there is a possibility may produce increase, discharge performance degradation, etc. of internal resistance.

[0004] Moreover, if the above-mentioned potassium-hydroxide water solution absorbs a carbon dioxide, since deterioration of the electrolytic solution will start by the reaction of  $2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3$  and the discharge engine performance will no longer be obtained, the life of a cell becomes short. Although to prepare the steam selective-absorption layer which absorbs a steam alternatively in the introduction hole of the air of a cell container, and to delay the transmission rate of a steam to it as this cure was tried, this steam selective-absorption layer had the problem that the capacity which absorbs a steam will be lost quickly, when the saturation state was reached. Moreover, invasion of a carbon dioxide was not able to be prevented by this approach.

[0005] Although a liquid spill is arranging paper, a nonwoven fabric, etc. and could be controlled to some extent to the air introduction hole of a cell container, there was no effectiveness of preventing receipts and payments of a steam and invasion of a carbon dioxide in these things. Although making an air intake extremely small and controlling receipts and payments of a steam and invasion of a carbon dioxide was also examined, since it was restricted to the amount of supply of oxygen in this case, there was a problem that the discharge engine performance fell victim. Moreover, by the above-mentioned approach, since neither receipts and payments of a steam nor invasion of a carbon dioxide could be prevented completely, many properties of a cell destabilized and it did not become fundamental solution of the problem that a life becomes short. And so, when the liquid spill by cubical expansion arose, the air intake was blockaded and there was also a problem that the

discharge engine performance was no longer obtained.

[0006] In order to incorporate oxygen in a cell container, preventing completely receipts and payments of a steam, and invasion of a carbon dioxide, the film which penetrates oxygen more preferentially than a steam and a carbon dioxide was required. However, generally, since the gas transmission rate of organic materials, such as a macromolecule, was in the inclination for the transmission rate of a steam or a carbon dioxide to be higher than the transmission rate of oxygen, development of the film which makes oxygen penetrate preferentially as compared with a steam or a carbon dioxide was not easy.

[0007] The hemoglobin contained in blood is excellent in the capacity which combines oxygen. For example, 1g hemoglobin combines 1.34ml oxygen under 37 degrees C and the conditions of atmospheric pressure. And although the above-mentioned hemoglobin combines oxygen about 100% in the high place of oxygen tension, once a partial pressure falls and oxygen begins to carry out desorption, it has the property of emitting oxygen quickly.

[0008] Then, using the oxygen transporter containing the metal complex which considers specific and reversible association as oxygen which imitated the above-mentioned hemoglobin was examined. There is the so-called liquid membrane which the porosity supporting lamella was infiltrated and film-ized the solution which dissolved the above-mentioned oxygen transporter in the suitable solvent to the thing typical as oxygen permselective membrane which used oxygen transporter.

[0009] However, in the above-mentioned liquid membrane, since a hydrophilic property was given to a porosity supporting lamella in order to infiltrate the above-mentioned solution good while the solvent which may dissolve oxygen transporter good is limited to the thing of hydrophilic properties, such as ethylene glycol, this liquid membrane had the problem that the effectiveness of preventing receipts and payments of a steam was inadequate. Moreover, since the dissolution rate of a carbon dioxide was quick, the organic solvent of the above-mentioned hydrophilic property of the effectiveness of preventing invasion of a carbon dioxide was also usually inadequate [ the liquid membrane concerned ].

[0010] The purpose of this invention is to stabilize many properties and offer a long lasting cell while it is excellent in the oxygen permselective membrane which can prevent more certainly receipts and payments of a steam, and invasion of a carbon dioxide while excelling in the capacity to make oxygen penetrate alternatively, and the discharge engine performance using it.

[0011]

[Means for Solving the Problem and its Function] Oxygen permselective membrane of this invention for solving the above-mentioned technical problem is characterized by film-izing the dispersion liquid which it is [ dispersion liquid ] hydrophobicity and distributed the solution of the oxygen transporter containing the metal complex which considers specific and reversible association as oxygen in the medium with the slow dissolution rate of a carbon dioxide.

[0012] Moreover, other oxygen permselective membrane of this invention is characterized by film-izing the oxygen resolvent which dissolves oxygen alternatively in the state of gel. Furthermore, the cell of this invention is characterized by making one side of the two above-mentioned sorts of oxygen permselective membrane intervene between this gas diffusion electrode and an air introduction hole while it prepares the gas diffusion electrode which uses oxygen as an active material along with the above-mentioned air introduction hole in the cell container which has the air introduction hole which leads to the open air.

[0013] The oxygen permselective membrane of this invention which consists of the above-mentioned configuration can also prevent more certainly receipts and payments of a steam, and invasion of a carbon dioxide while it is excellent in the capacity to make oxygen penetrate alternatively, because of what film-ized the dispersion liquid which it is [ dispersion liquid ] hydrophobicity and distributed the solution of oxygen transporter in the medium with the slow dissolution rate of a carbon dioxide. Moreover, like [ in the case of the liquid membrane which used the conventional organic solvent of a hydrophilic property ], in case a porosity supporting lamella is infiltrated and the above-mentioned dispersion liquid are film-ized, since it is not necessary to give a hydrophilic property to a porosity supporting lamella, there is also an advantage that there is no possibility that the effectiveness of preventing receipts and payments of a steam may fall.

[0014] Since the gel concerned will close the hole of a porosity supporting lamella when the above-mentioned dispersion liquid are furthermore film-ized in the condition of having gelled with the gelling agent swollen by the medium, the effectiveness of preventing receipts and payments of a steam and invasion of a carbon dioxide improves further. Moreover, since the gel concerned will close the hole of a porosity supporting lamella when other oxygen permselective membrane of this invention comes [ film ]-izing [ the oxygen resolvent which dissolves oxygen alternatively ] in the state of gel, and gel is infiltrated into a porosity supporting lamella like the conventional liquid membrane, for example, it film-izes, receipts and payments of a steam and invasion of a carbon dioxide are prevented certainly.

[0015] Moreover, since the porosity supporting lamella into which the above-mentioned gel is infiltrated does not need to give a hydrophilic property like before, receipts and payments of a steam and invasion of a carbon dioxide are certainly prevented also at this point. And even if it uses what gelled the oxygen resolvent as mentioned above under the high situation of the atmospheric temperature of the flame world of summer, a tropical area, etc., it does not evaporate simply, but it continues at a long period of time, and can maintain the film.

[0016] Therefore, since fluctuation of the concentration of the electrolytic solution by receipts and payments of a steam and the volume, degradation of the electrolytic solution by absorption of a carbon dioxide, etc. are more certainly prevented while excelling in the discharge engine performance, many properties stabilize and are long lasting [ the cell of this invention using one side of the two above-mentioned sorts of oxygen permselective membrane ]. This invention is explained below.

[0017] The oxygen permselective membrane which comes [ film ]-izing [ the dispersion liquid which it is / dispersion liquid / hydrophobicity and distributed the solution of the oxygen transporter containing the metal complex which considers specific and reversible association as the former oxygen among two sorts of oxygen permselective membrane of this invention first in the medium with the slow dissolution rate of a carbon dioxide ] is explained. Each various metal complex which has the function which considers specific and reversible association as oxygen as mentioned above as a metal complex which constitutes oxygen transporter is usable.

[0018] Complexes, such as cobalt of the compound which uses elements other than nitrogen, such as Schiff base compound; amino acid; amine system compound; sulfur, oxygen, and \*\*\*\*, as a coordination atom as an example of this metal complex although not limited to this, iron, manganese, palladium, and a rhodium, etc. are raised. 3-methoxy salcomine as a Schiff base compound, especially bis(salicylaldehyde) ethylene diimine cobalt (II) [common-name salcomines], 5-methoxy salcomine, 3-methyl salcomine, etc. are used suitably especially. Or the cobalt complex of a histidine or ammonia is also used suitably again.

[0019] If the above-mentioned metal complex is used together with an axial ligand, its function as oxygen transporter will improve further. As this axial ligand, although not limited to this, an imidazole, an amine, a pyridine, etc. are raised. A metal complex and an axial ligand are blended so that it may become equimolar. As a solvent for dissolving the above-mentioned oxygen transporter, each various solvent which may dissolve oxygen transporter is usable. As this solvent, although not limited to this, the solvent of the hydrophilic property of aprotic polar solvents, such as polyhydric alcohol; dimethyl sulfoxide (DMSO), such as lower alcohol; ethylene glycol, such as a water; methanol, ethanol, and isopropanol, and a diethylene glycol, and a diethyl formamide (DEF), etc. is raised.

[0020] The various media with the dissolution rate of a carbon dioxide slow as a medium which distributes the solution of oxygen transporter which are hydrophobicity can be used. although not limited to this as an example of this hydrophobic medium -- for example, fluorine-containing compounds, such as n-C eight F18, [104 degrees C of pel FURUORU normal-octane boiling points] pel FURUORU normal nonane [n-C nine F20, 123 degrees C of boiling points], pel FURUORU tributylamine [(C four F9) 3 N, 177 degrees C of boiling points], and perfluoropolyether [300 degrees C of boiling points], -- or silicone oil, such as dimethylsiloxane, etc. is raised.

[0021] In addition, as a hydrophobic medium, the high thing of the boiling point is especially used more suitably also in the above. It is because it does not evaporate even if it uses the high medium of the boiling point under the high situation of the atmospheric temperature of the flame world of

summer, a tropical area, etc., but it continues at a long period of time and the film can be maintained. In this invention, although especially the loadings of said oxygen transporter, a solvent, and a hydrophobic medium are not limited, as for oxygen transporter and a solvent, it is desirable to blend 0.07 or more millimols of oxygen transporter to one cc of solvents.

[0022] There is a possibility that the function in which the loadings of oxygen transporter penetrate oxygen alternatively under in the above-mentioned range may not fully be demonstrated. Moreover, although not limited especially about the upper limit of the loadings to the solvent of oxygen transporter, either, in order to raise an oxygen transmission rate, as there are many loadings of oxygen transporter, it is desirable and they can be blended in the operating temperature limits of a cell to the amount in which oxygen transporter does not deposit. In the case of the oxygen transporter and DMSO which were used in the examples 1-3 which this amount differs from oxygen transporter according to the class of solvent, for example, are mentioned later and which consist of a 3-methoxy salcomine complex and 4-dimethylaminopyridine, in 30 degrees C, it is possible to blend oxygen transporter up to 10 millimols to one cc DMSO.

[0023] In addition, especially in order to raise an oxygen transmission rate, as for the loadings of oxygen transporter, it is desirable that above-mentioned within the limits is also 0.5 to 5 millimol. As for especially the solution that dissolved oxygen transporter in the solvent at an above-mentioned rate, it is desirable to blend about 0.1-4 cc at a rate of about 0.3-2 cc to five cc of hydrophobic media.

[0024] There is a possibility that the function in which the loadings of the solution of the oxygen transporter to five cc of hydrophobic media penetrate oxygen alternatively under in the above-mentioned range may not fully be demonstrated. Conversely, when the loadings of the solution of oxygen transporter exceed the above-mentioned range, it becomes difficult to make homogeneity distribute the solution concerned in a hydrophobic medium, a solution and a medium carry out phase separation, and there is a possibility that it may become impossible to convey oxygen efficiently.

[0025] In order to distribute the solution of oxygen transporter in a hydrophobic medium, either mechanical means, such as supersonic vibration and \*\* to write, or the chemical means by addition of a surfactant, and both are adopted. In order to prevent receipts and payments of a steam, a hygroscopic low thing is desirable as much as possible, for example, although ionicity and nonionic various surfactants are usable as a surfactant, when it is a nonionic surfactant, 15 or less thing is suitably used for an HLB value.

[0026] Although an HLB value is not limited to this as an example of the nonionic surfactant which is 15 or less, sorbitan trioleate (HLB value 1.8), sorbitan tristearate (HLB value 2.1), glycerol monostearate (HLB value 3.8), sorbitan monooleate (HLB value 4.3), sorbitan monostearate (HLB value 4.7), sorbitan monopalmitate (HLB value 6.7), etc. are raised.

[0027] Moreover, if an anionic surfactant is used when using the complex of copper or cobalt as oxygen transporter, a membranous oxygen transmission rate can be improved further. This is that the anion site of the anionic surface active agent which stuck to the interface of the solution which dissolved the above-mentioned oxygen transporter, and the hydrophobic dispersion medium which distributed this solution condenses the copper ion in a solution, and cobalt ion to the above-mentioned interface by the electrostatic interaction, and it is considered to be the cause to make the reaction rate of the adsorption reaction of the oxygen by oxygen transporter in the interface concerned increase.

[0028] Although not limited especially about the loadings of a surfactant, it is desirable that it is about 0.01-0.1g to one cc of hydrophobic media. When there is a possibility that the loadings of a surfactant may become inadequate [ under the above-mentioned range / the addition effectiveness ], and cannot fully distribute oxygen transporter in a hydrophobic medium and the loadings of a surfactant exceed the above-mentioned range conversely, there is a possibility that a steam may become easy to invade and the permselectivity of oxygen may fall.

[0029] In addition, as for especially the loadings of a surfactant, it is desirable that above-mentioned within the limits is also 0.03-0.08g. What is necessary is to infiltrate a porosity supporting lamella and just to film-ize dispersion liquid like the conventional liquid membrane, in order to film-ize the dispersion liquid which consist of each above-mentioned component. The cross section of an example of the oxygen permselective membrane of the above-mentioned structure is shown in

drawing 1 .

[0030] The oxygen permselective membrane A of drawing infiltrates dispersion liquid 2 into through-hole 12a of the above-mentioned porous layer 12 of the porosity supporting lamella 1 which consists of a base film 11 and a porous layer 12 formed in the one side, and is film-ized. In the above-mentioned oxygen permselective membrane A, after the solution of the oxygen transporter distributed in dispersion liquid 2 adsorbs oxygen alternatively by the gas supply side (it sets to drawing and is the bottom) of the film which is a hyperoxia partial pressure, the inside of dispersion liquid 2 is diffused and oxygen is alternatively penetrated by the process in which desorption of the oxygen is carried out by the transparency side (it sets to drawing and is the bottom) of the film which is a hypoxia partial pressure.

[0031] As a base film 11 which constitutes the porosity supporting lamella 1 among the above-mentioned oxygen permselective membrane A, it excels in the permeability of oxygen and what moreover does not pass dispersion liquid 2, the electrolytic solution of a cell, or a steam is used suitably. Although not limited to this as this base film 11, too, the permeability of oxygen is good for one side of a film which has the very fine through-hole which is water repellence in itself [, such as porous polytetrafluoroethylene (PTFE) film, ], and was excellent in the permeability of oxygen, and what carried out the laminating of the dispersion-liquid transparency prevention layer which consists of the quality of the material which does not melt into hydrophobic media which moreover constitute dispersion liquid, such as silicone rubber, is raised to it.

[0032] the base film 11 of the above-mentioned two-layer structure -- setting -- a water-repellent film -- a liquid spill of the electrolytic solution -- or it functions in order to prevent passage of a steam, and a dispersion-liquid transparency prevention layer functions in order to prevent passage of dispersion liquid 2. Moreover, as a porous layer 12 formed in one side (near field in which the dispersion-liquid transparency prevention layer was formed preferably) of the above-mentioned base film 11, the film which consists of water-repellent ingredients which have much through-hole 12a, such as PTFE, is used suitably.

[0033] The thickness of this porous layer 12 is equivalent to the thickness of the film (liquid membrane) of dispersion liquid 2 so that clearly from drawing 1 . The thickness of liquid membrane Since it is an element important when opting for the function to penetrate the oxygen in the oxygen permselective membrane A alternatively, and to prevent receipts and payments of a steam, and invasion of a carbon dioxide According to each above-mentioned property for which the oxygen permselective membrane A is asked, especially the range of concrete thickness is not limited that what is necessary is just to set up the optimal range.

[0034] However, as for the thickness of the above-mentioned porous layer 12, generally, it is desirable that it is within the limits of 5-200 micrometers. When a possibility that the capacity for the amount of the dispersion liquid held at the porous layer 12 concerned to decrease under in the above-mentioned range, and to penetrate oxygen alternatively, and to prevent receipts and payments of a steam and invasion of a carbon dioxide may decline arises and the thickness of a porous layer 12 exceeds the above-mentioned range conversely, the distance of through-hole 12a becomes long, and a possibility that the capacity which penetrates oxygen may decline arises. In addition, as for especially the thickness of a porous layer 12, it is desirable that above-mentioned within the limits is also 1.5-10 micrometers.

[0035] Moreover, although limited also neither about the aperture of through-hole 12a in the above-mentioned porous layer 12, nor especially the voidage of the whole porous layer 12, the aperture of through-hole 12a is expressed with an average aperture, its about 0.01-10 micrometers are desirable, and about 20 - 90% of the voidage of a porous layer 12 is desirable. Although the average aperture of through-hole 12a is based also on the thickness of a porous layer 12 under in the above-mentioned range, a possibility in the oxygen permselective membrane A that the capacity which penetrates oxygen may decline arises. Moreover, conversely, when the average aperture of through-hole 12a exceeds the above-mentioned range, a possibility that the capacity for the through-hole 12a concerned to hold dispersion liquid 2 may decline, it may become impossible to form liquid membrane as shown in drawing 1 therefore, and it may become impossible to prevent receipts and payments of a steam and invasion of a carbon dioxide with the surface tension of dispersion liquid 2 arises. In addition, as for especially the average aperture of through-hole 12a, it is desirable that



above-mentioned within the limits is also 0.1-5 micrometers.

[0036] On the other hand, when a possibility that the capacity for the amount of the dispersion liquid which can sink in into the porous layer 12 concerned to decrease under in said range, and to penetrate oxygen alternatively, and to prevent receipts and payments of a steam and invasion of a carbon dioxide may decline arises and the voidage of a porous layer 12 exceeds said range conversely, there is a possibility that the reinforcement of a porous layer 12 may become inadequate. In addition, above-mentioned within the limits of about 40 - 80% of especially the voidage of a porous layer 12 is also desirable.

[0037] Since gel will close the hole of a porous layer 12 as mentioned above when the dispersion liquid 2 into which the above-mentioned porous layer 12 is infiltrated are gelled, the effectiveness of preventing the receipts and payments of a steam and the invasion of a carbon dioxide in the oxygen permselective membrane A improves further. Although each well-known various gelling agent can use it conventionally in order to gel dispersion liquid 2, the so-called resin of the oil absorption nature which absorbs and gels the hydrophobic medium which constitutes the dispersion liquid 2 concerned especially is suitably used as a gelling agent.

[0038] the bridging object of a low consistency of the polymer which made the oleophilic monomer the base unit as resin of this oil absorption nature although not limited to this -- or poly NORUBONENGOMU to which ring opening polymerization of NORUBONEN was carried out is raised. Although various approaches can be considered to gel the dispersion liquid 2 into which a porous layer 12 is infiltrated using the resin of the above-mentioned oil absorption nature Apply to the front face of a porous layer 12 the solution which contains the resin of oil absorption nature first, and after making it sink in into through-hole 12a of the porous layer 12 concerned, heating and drying and removing a solvent, dispersion liquid 2 are applied to the front face of the above-mentioned porous layer 12. Since the approach of making absorb dispersion liquid 2 and gelling in the resin of oil absorption nature with which it sank in into through-hole 12a is easy a process and can moreover be certainly filled up with gel in through-hole 12a, it is adopted suitably.

[0039] The oxygen permselective membrane which film-ized next the oxygen resolvent which dissolves the latter oxygen alternatively among two sorts of oxygen permselective membrane of this invention in the state of gel is explained. As an oxygen resolvent used by this invention, each various compound which dissolves oxygen alternatively as mentioned above is usable. As an example of this oxygen resolvent, although not limited to this, a perfluoro-butylamine etc. is raised.

[0040] A gelling agent is used in order to gel the above-mentioned oxygen resolvent. As a gelling agent, although each organic or inorganic conventionally well-known various ingredient is usable, especially absorptivity resin is used suitably. In order to film-ize the oxygen resolvent gelled with the above-mentioned gelling agent, various approaches can be considered, but while infiltrating a porosity supporting lamella and film-izing the gel concerned like the conventional liquid membrane raises an oxygen transmission rate, when maintaining membranous reinforcement, it is desirable.

[0041] As a porosity supporting lamella, what consists of a base film 11 and a porous layer 12 formed in the one side is suitably used so that it may be shown in having illustrated by previous oxygen permselective membrane, and the same thing, i.e., drawing 1 . Although various approaches can be considered using the above-mentioned porosity supporting lamella 1 to film-ize gel of an oxygen resolvent Apply to the front face of a porous layer 12 the solution which contains the resin of absorptivity first, and make it sink in into through-hole 12a of the porous layer 12 concerned, and after heating and drying and removing a solvent, an oxygen resolvent is supplied to the front face of the above-mentioned porous layer 12. Since the approach of making absorb an oxygen resolvent and gelling in the resin of absorptivity with which it sank in into through-hole 12a is easy a process and can moreover be certainly filled up with gel in through-hole 12a, it is adopted suitably.

[0042] Although two sorts of oxygen permselective membrane [ each ] of this invention explained above can be used in various fields, such as an oxygen permeable membrane, it is especially used suitably as oxygen permselective membrane of a cell. Below, the cell of this invention which used the above-mentioned oxygen permselective membrane is explained. The configuration of this invention is applicable to various cells with the need of using oxygen permselective membrane. While preparing the gas diffusion electrode which uses oxygen as an active material along with the above-mentioned air introduction hole in the cell container which has in more detail the air

introduction hole which leads to the open air, it is applicable to the cell of various methods which made oxygen permselective membrane intervene between this gas diffusion electrode and an air introduction hole. An air cell and a fuel cell are raised as this cell.

[0043] The cross section of one example of the air cell as a cell of this invention is shown in drawing 2. The cell B of drawing 2 carries out the laminating of the gas diffusion electrode 5, the diaphragm 6, and negative electrode 7 as the oxygen permselective membrane A, the \*\*\*\* water screen 4, and a positive electrode to order from a side-face [ in which the above-mentioned air introduction hole 31a was formed in the cell container 3 which prepared air introduction hole 31a which is well-informed about the open air in the one side face ] side. In addition, the above-mentioned air introduction hole 31a is formed, and the cell container 3 consists of a positive-electrode container 31 electrically connected with the gas diffusion electrode 5, and a negative electrode 7 and the negative-electrode container 32 connected electrically. It is sealed by the insulating gasket 8 between the above-mentioned positive-electrode container 31 and the negative-electrode container 32. Moreover, the diaphragm 6 has two-layer structure of the 1st and 2nd diaphragms 61 and 62.

[0044] As oxygen permselective membrane A, one side of two sorts of oxygen permselective membrane of this invention mentioned above is used among the above. This oxygen permselective membrane A is arranged, where it turned to the air introduction hole 31a side the porous layer 12 into which dispersion liquid 2 (or gel which made the oxygen solvent swell) were infiltrated and a base film 11 is turned to the \*\*\*\* water screen 4 side. The porous PTFE film same with having used it by the base film 11 as the \*\*\*\* water screen 4 etc. is used.

[0045] A gas diffusion electrode 5, a diaphragm 6, and a negative electrode 7 are constituted as usual. Moreover, as mentioned above, the electrolytic solutions, such as a potassium-hydroxide water solution, sink into a diaphragm 6. In addition, it is constituted as usual by the fuel cell.

[0046]

[Example] This invention is explained based on an example below.

0.3g of oxygen transporter which consists of an example 13-methoxy salcomine complex and 4-dimethylaminopyridine of equimolar was dissolved in one cc DMSO, the solution was produced, with 0.05g (a fatty-acid ethylene oxide addition product, HLB values 13.2-13.5) of nonionic surfactants, this solution was added to five cc perfluoropolyether, was written, was \*(ed), and dispersion liquid were produced.

[0047] As shown in drawing 1, after infiltrating these dispersion liquid 2 into the porous layer 12 (voidage of 40%, thickness of 10 micrometers) made from PTFE which has through-hole 12a of 0.22 micrometers of a majority of average apertures next, the oxygen permselective membrane A of an example 1 was laminating-manufactured by using this porous layer 12 as a base film 11. In addition, as a base film 11, addition reaction mold silicone rubber is applied to one side of a porous PTFE film (the average aperture of 0.1 micrometers, thickness of 50 micrometers), the hardening reaction was carried out, the thing in which the dispersion-liquid transparency prevention layer of 60 micrometers of thickness was formed was used, and the laminating of the porous layer 12 was carried out on this dispersion-liquid transparency prevention layer.

The oxygen permselective membrane A of an example 2 was manufactured like the example 1 except having set thickness of example 2 porous layer 12 to 110 micrometers.

having used it in the example 3 example 1 -- the same -- after having applied the solution of oil absorption nature resin [the trade name "OREOSOBUSL-130" by NIPPON SHOKUBAI Co., Ltd.] to the front face of the porous layer 12 with a thickness of 10 micrometers so that it might become the thickness of 5 micrometers by the bar coat method, and infiltrating through-hole 12a of a porous layer 12 into it, it was made to dry for 5 minutes at 100 degrees C

[0048] Subsequently, after having supplied the same dispersion liquid 2 as having used it for this porous layer 12 in the example 1, making the oil absorption nature resin with which it sank in into through-hole 12a absorb and gelling, the oxygen permselective membrane A of an example 3 was laminating-manufactured by using this porous layer 12 as the same base film 11 as having used it in the example 1.

having used it in the example 4 example 1 -- the same -- after having applied the solution of absorptivity resin [the trade name "AKUAYUKU" by Sumitomo Seika Chemicals Co., Ltd.] to the front face of the porous layer 12 with a thickness of 10 micrometers so that it might become the

thickness of 10 micrometers by the bar coat method, and infiltrating through-hole 12a of a porous layer 12 into it, it was made to dry for 15 minutes at 70 degrees C

[0049] Subsequently, this porous layer 12 was immersed for 5 minutes into the 20 cc perfluorobutylamine which is an oxygen solvent, and after making the perfluorobutylamine absorb in absorptivity resin and gelling it, the oxygen permselective membrane A of an example 4 was laminating-manufactured by using this porous layer 12 as the same base film 11 as having used it in the example 1. The cel for measurement is equipped with the oxygen permselective membrane A of each above-mentioned example, and they are the temperature of 25 degrees C, and the pressure of 1.2kg/cm<sup>2</sup> to the porous layer 12 side. When air was supplied, the gas chromatography analyzed the presentation of the gas penetrated to the base film 11 side of the oxygen permselective membrane A concerned.

[0050] And from the analysis result, the separation factor alpha (O<sub>2</sub>/CO<sub>2</sub>) of the oxygen to the separation factor alpha (O<sub>2</sub>/H<sub>2</sub>O) and carbon dioxide of oxygen to transmission rate [ of oxygen ] Q (O<sub>2</sub>) [cm<sup>3</sup> / cm<sup>2</sup>, and sec-cmHg] and a steam was computed. A result is shown in Table 1.

[0051]

[Table 1]

	Q (O <sub>2</sub> )	$\alpha$ (O <sub>2</sub> /H <sub>2</sub> O)	$\alpha$ (O <sub>2</sub> /CO <sub>2</sub> )
実施例 1	$5 \times 10^{-3}$	1 2	1 1
実施例 2	$20 \times 10^{-4}$	2 0	1 8
実施例 3	$8 \times 10^{-3}$	8	7
実施例 4	$7 \times 10^{-3}$	1 0	1 9

[0052] It included in the carbon button mold air cell (the diameter of 11.6mm, height of 5.4mm, R44 size) which shows the oxygen permselective membrane A manufactured in the example 5 example 1 to drawing 2 . And when the load of 15kohm was connected to the above-mentioned carbon button mold air cell under conditions of the temperature of 20 degrees C, and 70% of relative humidity and continuous discharge was performed, as a continuous line showed, compared with the case (a drawing destructive line shows) where the oxygen permselective membrane A is not incorporated, reinforcement was able to be carried out to drawing 3 about twice.

[0053]

[Effect of the Invention] As mentioned above, as explained in full detail, the oxygen permselective membrane of this invention can also prevent more certainly receipts and payments of a steam, and invasion of a carbon dioxide while it is excellent in the capacity to make oxygen penetrate alternatively. Therefore, many properties stabilize and are long lasting while the cell of this invention using the above-mentioned oxygen permselective membrane is excellent in the discharge engine performance, and it can be especially equal to prolonged use and storage.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing an example of the structure of the oxygen permselective membrane of this invention.

[Drawing 2] It is the sectional view using the above-mentioned oxygen permselective membrane showing an example of the structure of the cell of this invention.

[Drawing 3] It is the graph which shows the measurement result of the life of the cell manufactured in the example 5 of this invention.

[Description of Notations]

A Oxygen permselective membrane

1 Porosity Supporting Lamella

2 Dispersion Liquid

B Cell

3 Cell Container

31 Air Introduction Hole

5 Gas Diffusion Electrode

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the oxygen permselective membrane which has the function which penetrates oxygen gas alternatively, and cells using it, such as an air cell and a fuel cell.

[0002]

[Description of the Prior Art] Generally in the cell equipped with the gas diffusion electrode which uses oxygen, such as the above-mentioned air cell and a fuel cell, for an active material, using the oxygen in the air which prepared the air introduction hole which leads to the open air, and was adopted from here for a cell container as an active material is performed. Although many properties of the above-mentioned cell, such as internal resistance of a cell and a discharge property, are stable in extent with which practical use is presented, the much more stability and reinforcement are desired and the development to reinforcement is continued.

[0003] for example, fluctuation of the concentration of the electrolytic solution in a cell by a steam going in and out from the introduction hole of air, as for the conventional cell, and the volume -- or there is a possibility by absorption of the carbon dioxide which invaded from the introduction hole of the above-mentioned air that degradation of the electrolytic solution etc. may arise. For example, as a result of this electrolytic solution's incorporating external moisture and producing a concentration fall and cubical expansion if relative humidity is higher than 45 - 59% when the potassium-hydroxide water solution whose concentration is about 30 - 35% is used as the electrolytic solution, there is a possibility may produce discharge performance degradation, the leakage of the electrolytic solution, etc., when relative humidity is conversely lower than the above-mentioned range, evaporation of the electrolytic solution starts and there is a possibility may produce increase, discharge performance degradation, etc. of internal resistance.

[0004] Moreover, if the above-mentioned potassium-hydroxide water solution absorbs a carbon dioxide, since deterioration of the electrolytic solution will start by the reaction of  $2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3$  and the discharge engine performance will no longer be obtained, the life of a cell becomes short. Although to prepare the steam selective-absorption layer which absorbs a steam alternatively in the introduction hole of the air of a cell container, and to delay the transmission rate of a steam to it as this cure was tried, this steam selective-absorption layer had the problem that the capacity which absorbs a steam will be lost quickly, when the saturation state was reached. Moreover, invasion of a carbon dioxide was not able to be prevented by this approach.

[0005] Although a liquid spill is arranging paper, a nonwoven fabric, etc. and could be controlled to some extent to the air introduction hole of a cell container, there was no effectiveness of preventing receipts and payments of a steam and invasion of a carbon dioxide in these things. Although making an air intake extremely small and controlling receipts and payments of a steam and invasion of a carbon dioxide was also examined, since it was restricted to the amount of supply of oxygen in this case, there was a problem that the discharge engine performance fell victim. Moreover, by the above-mentioned approach, since neither receipts and payments of a steam nor invasion of a carbon dioxide could be prevented completely, many properties of a cell destabilized and it did not become fundamental solution of the problem that a life becomes short. And so, when the liquid spill by cubical expansion arose, the air intake was blockaded and there was also a problem that the

discharge engine performance was no longer obtained.

[0006] In order to incorporate oxygen in a cell container, preventing completely receipts and payments of a steam, and invasion of a carbon dioxide, the film which penetrates oxygen more preferentially than a steam and a carbon dioxide was required. However, generally, since the gas transmission rate of organic materials, such as a macromolecule, was in the inclination for the transmission rate of a steam or a carbon dioxide to be higher than the transmission rate of oxygen, development of the film which makes oxygen penetrate preferentially as compared with a steam or a carbon dioxide was not easy.

[0007] The hemoglobin contained in blood is excellent in the capacity which combines oxygen. For example, 1g hemoglobin combines 1.34ml oxygen under 37 degrees C and the conditions of atmospheric pressure. And although the above-mentioned hemoglobin combines oxygen about 100% in the high place of oxygen tension, once a partial pressure falls and oxygen begins to carry out desorption, it has the property of emitting oxygen quickly.

[0008] Then, using the oxygen transporter containing the metal complex which considers specific and reversible association as oxygen which imitated the above-mentioned hemoglobin was examined. There is the so-called liquid membrane which the porosity supporting lamella was infiltrated and film-ized the solution which dissolved the above-mentioned oxygen transporter in the suitable solvent to the thing typical as oxygen permselective membrane which used oxygen transporter.

[0009] However, in the above-mentioned liquid membrane, since a hydrophilic property was given to a porosity supporting lamella in order to infiltrate the above-mentioned solution good while the solvent which may dissolve oxygen transporter good is limited to the thing of hydrophilic properties, such as ethylene glycol, this liquid membrane had the problem that the effectiveness of preventing receipts and payments of a steam was inadequate. Moreover, since the dissolution rate of a carbon dioxide was quick, the organic solvent of the above-mentioned hydrophilic property of the effectiveness of preventing invasion of a carbon dioxide was also usually inadequate [ the liquid membrane concerned ].

[0010] The purpose of this invention is to stabilize many properties and offer a long lasting cell while it is excellent in the oxygen permselective membrane which can prevent more certainly receipts and payments of a steam, and invasion of a carbon dioxide while excelling in the capacity to make oxygen penetrate alternatively, and the discharge engine performance using it.

[0011]

[Means for Solving the Problem and its Function] Oxygen permselective membrane of this invention for solving the above-mentioned technical problem is characterized by film-izing the dispersion liquid which it is [ dispersion liquid ] hydrophobicity and distributed the solution of the oxygen transporter containing the metal complex which considers specific and reversible association as oxygen in the medium with the slow dissolution rate of a carbon dioxide.

[0012] Moreover, other oxygen permselective membrane of this invention is characterized by film-izing the oxygen resolvent which dissolves oxygen alternatively in the state of gel. Furthermore, the cell of this invention is characterized by making one side of the two above-mentioned sorts of oxygen permselective membrane intervene between this gas diffusion electrode and an air introduction hole while it prepares the gas diffusion electrode which uses oxygen as an active material along with the above-mentioned air introduction hole in the cell container which has the air introduction hole which leads to the open air.

[0013] The oxygen permselective membrane of this invention which consists of the above-mentioned configuration can also prevent more certainly receipts and payments of a steam, and invasion of a carbon dioxide while it is excellent in the capacity to make oxygen penetrate alternatively, because of what film-ized the dispersion liquid which it is [ dispersion liquid ] hydrophobicity and distributed the solution of oxygen transporter in the medium with the slow dissolution rate of a carbon dioxide. Moreover, like [ in the case of the liquid membrane which used the conventional organic solvent of a hydrophilic property ], in case a porosity supporting lamella is infiltrated and the above-mentioned dispersion liquid are film-ized, since it is not necessary to give a hydrophilic property to a porosity supporting lamella, there is also an advantage that there is no possibility that the effectiveness of preventing receipts and payments of a steam may fall.

[0014] Since the gel concerned will close the hole of a porosity supporting lamella when the above-mentioned dispersion liquid are furthermore film-ized in the condition of having gelled with the gelling agent swollen by the medium, the effectiveness of preventing receipts and payments of a steam and invasion of a carbon dioxide improves further. Moreover, since the gel concerned will close the hole of a porosity supporting lamella when other oxygen permselective membrane of this invention comes [ film ]-izing [ the oxygen resolvent which dissolves oxygen alternatively ] in the state of gel, and gel is infiltrated into a porosity supporting lamella like the conventional liquid membrane, for example, it film-izes, receipts and payments of a steam and invasion of a carbon dioxide are prevented certainly.

[0015] Moreover, since the porosity supporting lamella into which the above-mentioned gel is infiltrated does not need to give a hydrophilic property like before, receipts and payments of a steam and invasion of a carbon dioxide are certainly prevented also at this point. And even if it uses what gelled the oxygen resolvent as mentioned above under the high situation of the atmospheric temperature of the flame world of summer, a tropical area, etc., it does not evaporate simply, but it continues at a long period of time, and can maintain the film.

[0016] Therefore, since fluctuation of the concentration of the electrolytic solution by receipts and payments of a steam and the volume, degradation of the electrolytic solution by absorption of a carbon dioxide, etc. are more certainly prevented while excelling in the discharge engine performance, many properties stabilize and are long lasting [ the cell of this invention using one side of the two above-mentioned sorts of oxygen permselective membrane ]. This invention is explained below.

[0017] The oxygen permselective membrane which comes [ film ]-izing [ the dispersion liquid which it is / dispersion liquid / hydrophobicity and distributed the solution of the oxygen transporter containing the metal complex which considers specific and reversible association as the former oxygen among two sorts of oxygen permselective membrane of this invention first in the medium with the slow dissolution rate of a carbon dioxide ] is explained. Each various metal complex which has the function which considers specific and reversible association as oxygen as mentioned above as a metal complex which constitutes oxygen transporter is usable.

[0018] Complexes, such as cobalt of the compound which uses elements other than nitrogen, such as Schiff base compound; amino acid; amine system compound; sulfur, oxygen, and \*\*\*\*, as a coordination atom as an example of this metal complex although not limited to this, iron, manganese, palladium, and a rhodium, etc. are raised. 3-methoxy salcomine as a Schiff base compound, especially bis(salichlaldehyde) ethylene diimine cobalt (II) [common-name salcomines], 5-methoxy salcomine, 3-methyl salcomine, etc. are used suitably especially. Or the cobalt complex of a histidine or ammonia is also used suitably again.

[0019] If the above-mentioned metal complex is used together with an axial ligand, its function as oxygen transporter will improve further. As this axial ligand, although not limited to this, an imidazole, an amine, a pyridine, etc. are raised. A metal complex and an axial ligand are blended so that it may become equimolar. As a solvent for dissolving the above-mentioned oxygen transporter, each various solvent which may dissolve oxygen transporter is usable. As this solvent, although not limited to this, the solvent of the hydrophilic property of aprotic polar solvents, such as polyhydric-alcohol; dimethyl sulfoxide (DMSO), such as lower alcohol; ethylene glycol, such as a water; methanol, ethanol, and isopropanol, and a diethylene glycol, and a diethyl formamide (DEF), etc. is raised.

[0020] The various media with the dissolution rate of a carbon dioxide slow as a medium which distributes the solution of oxygen transporter which are hydrophobicity can be used. although not limited to this as an example of this hydrophobic medium -- for example, fluorine-containing compounds, such as n-C eight F18, [104 degrees C of pel FURUORU normal-octane boiling points] pel FURUORU normal nonane [n-C nine F20, 123 degrees C of boiling points], pel FURUORU tributylamine [(C four F9) 3 N, 177 degrees C of boiling points], and perfluoropolyether [300 degrees C of boiling points], -- or silicone oil, such as dimethylsiloxane, etc. is raised.

[0021] In addition, as a hydrophobic medium, the high thing of the boiling point is especially used more suitably also in the above. It is because it does not evaporate even if it uses the high medium of the boiling point under the high situation of the atmospheric temperature of the flame world of

summer, a tropical area, etc., but it continues at a long period of time and the film can be maintained. In this invention, although especially the loadings of said oxygen transporter, a solvent, and a hydrophobic medium are not limited, as for oxygen transporter and a solvent, it is desirable to blend 0.07 or more millimols of oxygen transporter to one cc of solvents.

[0022] There is a possibility that the function in which the loadings of oxygen transporter penetrate oxygen alternatively under in the above-mentioned range may not fully be demonstrated. Moreover, although not limited especially about the upper limit of the loadings to the solvent of oxygen transporter, either, in order to raise an oxygen transmission rate, as there are many loadings of oxygen transporter, it is desirable and they can be blended in the operating temperature limits of a cell to the amount in which oxygen transporter does not deposit. In the case of the oxygen transporter and DMSO which were used in the examples 1-3 which this amount differs from oxygen transporter according to the class of solvent, for example, are mentioned later and which consist of a 3-methoxy salcomine complex and 4-dimethylaminopyridine, in 30 degrees C, it is possible to blend oxygen transporter up to 10 millimols to one cc DMSO.

[0023] In addition, especially in order to raise an oxygen transmission rate, as for the loadings of oxygen transporter, it is desirable that above-mentioned within the limits is also 0.5 to 5 millimol. As for especially the solution that dissolved oxygen transporter in the solvent at an above-mentioned rate, it is desirable to blend about 0.1-4 cc at a rate of about 0.3-2 cc to five cc of hydrophobic media.

[0024] There is a possibility that the function in which the loadings of the solution of the oxygen transporter to five cc of hydrophobic media penetrate oxygen alternatively under in the above-mentioned range may not fully be demonstrated. Conversely, when the loadings of the solution of oxygen transporter exceed the above-mentioned range, it becomes difficult to make homogeneity distribute the solution concerned in a hydrophobic medium, a solution and a medium carry out phase separation, and there is a possibility that it may become impossible to convey oxygen efficiently.

[0025] In order to distribute the solution of oxygen transporter in a hydrophobic medium, either mechanical means, such as supersonic vibration and \*\* to write, or the chemical means by addition of a surfactant, and both are adopted. In order to prevent receipts and payments of a steam, a hygroscopic low thing is desirable as much as possible, for example, although ionicity and nonionic various surfactants are usable as a surfactant, when it is a nonionic surfactant, 15 or less thing is suitably used for an HLB value.

[0026] Although an HLB value is not limited to this as an example of the nonionic surfactant which is 15 or less, sorbitan trioleate (HLB value 1.8), sorbitan tristearate (HLB value 2.1), glycerol monostearate (HLB value 3.8), sorbitan monooleate (HLB value 4.3), sorbitan monostearate (HLB value 4.7), sorbitan monopalmitate (HLB value 6.7), etc. are raised.

[0027] Moreover, if an anionic surfactant is used when using the complex of copper or cobalt as oxygen transporter, a membranous oxygen transmission rate can be improved further. This is that the anion site of the anionic surface active agent which stuck to the interface of the solution which dissolved the above-mentioned oxygen transporter, and the hydrophobic dispersion medium which distributed this solution condenses the copper ion in a solution, and cobalt ion to the above-mentioned interface by the electrostatic interaction, and it is considered to be the cause to make the reaction rate of the adsorption reaction of the oxygen by oxygen transporter in the interface concerned increase.

[0028] Although not limited especially about the loadings of a surfactant, it is desirable that it is about 0.01-0.1g to one cc of hydrophobic media. When there is a possibility that the loadings of a surfactant may become inadequate [ under the above-mentioned range / the addition effectiveness ], and cannot fully distribute oxygen transporter in a hydrophobic medium and the loadings of a surfactant exceed the above-mentioned range conversely, there is a possibility that a steam may become easy to invade and the permselectivity of oxygen may fall.

[0029] In addition, as for especially the loadings of a surfactant, it is desirable that above-mentioned within the limits is also 0.03-0.08g. What is necessary is to infiltrate a porosity supporting lamella and just to film-ize dispersion liquid like the conventional liquid membrane, in order to film-ize the dispersion liquid which consist of each above-mentioned component. The cross section of an example of the oxygen permselective membrane of the above-mentioned structure is shown in



drawing 1 .

[0030] The oxygen permselective membrane A of drawing infiltrates dispersion liquid 2 into through-hole 12a of the above-mentioned porous layer 12 of the porosity supporting lamella 1 which consists of a base film 11 and a porous layer 12 formed in the one side, and is film-ized. In the above-mentioned oxygen permselective membrane A, after the solution of the oxygen transporter distributed in dispersion liquid 2 adsorbs oxygen alternatively by the gas supply side (it sets to drawing and is the bottom) of the film which is a hyperoxia partial pressure, the inside of dispersion liquid 2 is diffused and oxygen is alternatively penetrated by the process in which desorption of the oxygen is carried out by the transparency side (it sets to drawing and is the bottom) of the film which is a hypoxia partial pressure.

[0031] As a base film 11 which constitutes the porosity supporting lamella 1 among the above-mentioned oxygen permselective membrane A, it excels in the permeability of oxygen and what moreover does not pass dispersion liquid 2, the electrolytic solution of a cell, or a steam is used suitably. Although not limited to this as this base film 11, too, the permeability of oxygen is good for one side of a film which has the very fine through-hole which is water repellence in itself [, such as porous polytetrafluoroethylene (PTFE) film, ], and was excellent in the permeability of oxygen, and what carried out the laminating of the dispersion-liquid transparency prevention layer which consists of the quality of the material which does not melt into hydrophobic media which moreover constitute dispersion liquid, such as silicone rubber, is raised to it.

[0032] the base film 11 of the above-mentioned two-layer structure -- setting -- a water-repellent film -- a liquid spill of the electrolytic solution -- or it functions in order to prevent passage of a steam, and a dispersion-liquid transparency prevention layer functions in order to prevent passage of dispersion liquid 2. Moreover, as a porous layer 12 formed in one side (near field in which the dispersion-liquid transparency prevention layer was formed preferably) of the above-mentioned base film 11, the film which consists of water-repellent ingredients which have much through-hole 12a, such as PTFE, is used suitably.

[0033] The thickness of this porous layer 12 is equivalent to the thickness of the film (liquid membrane) of dispersion liquid 2 so that clearly from drawing 1 . The thickness of liquid membrane Since it is an element important when opting for the function to penetrate the oxygen in the oxygen permselective membrane A alternatively, and to prevent receipts and payments of a steam, and invasion of a carbon dioxide According to each above-mentioned property for which the oxygen permselective membrane A is asked, especially the range of concrete thickness is not limited that what is necessary is just to set up the optimal range.

[0034] However, as for the thickness of the above-mentioned porous layer 12, generally, it is desirable that it is within the limits of 5-200 micrometers. When a possibility that the capacity for the amount of the dispersion liquid held at the porous layer 12 concerned to decrease under in the above-mentioned range, and to penetrate oxygen alternatively, and to prevent receipts and payments of a steam and invasion of a carbon dioxide may decline arises and the thickness of a porous layer 12 exceeds the above-mentioned range conversely, the distance of through-hole 12a becomes long, and a possibility that the capacity which penetrates oxygen may decline arises. In addition, as for especially the thickness of a porous layer 12, it is desirable that above-mentioned within the limits is also 1.5-10 micrometers.

[0035] Moreover, although limited also neither about the aperture of through-hole 12a in the above-mentioned porous layer 12, nor especially the voidage of the whole porous layer 12, the aperture of through-hole 12a is expressed with an average aperture, its about 0.01-10 micrometers are desirable, and about 20 - 90% of the voidage of a porous layer 12 is desirable. Although the average aperture of through-hole 12a is based also on the thickness of a porous layer 12 under in the above-mentioned range, a possibility in the oxygen permselective membrane A that the capacity which penetrates oxygen may decline arises. Moreover, conversely, when the average aperture of through-hole 12a exceeds the above-mentioned range, a possibility that the capacity for the through-hole 12a concerned to hold dispersion liquid 2 may decline, it may become impossible to form liquid membrane as shown in drawing 1 therefore, and it may become impossible to prevent receipts and payments of a steam and invasion of a carbon dioxide with the surface tension of dispersion liquid 2 arises. In addition, as for especially the average aperture of through-hole 12a, it is desirable that

above-mentioned within the limits is also 0.1-5 micrometers.

[0036] On the other hand, when a possibility that the capacity for the amount of the dispersion liquid which can sink in into the porous layer 12 concerned to decrease under in said range, and to penetrate oxygen alternatively, and to prevent receipts and payments of a steam and invasion of a carbon dioxide may decline arises and the voidage of a porous layer 12 exceeds said range conversely, there is a possibility that the reinforcement of a porous layer 12 may become inadequate. In addition, above-mentioned within the limits of about 40 - 80% of especially the voidage of a porous layer 12 is also desirable.

[0037] Since gel will close the hole of a porous layer 12 as mentioned above when the dispersion liquid 2 into which the above-mentioned porous layer 12 is infiltrated are gelled, the effectiveness of preventing the receipts and payments of a steam and the invasion of a carbon dioxide in the oxygen permselective membrane A improves further. Although each well-known various gelling agent can use it conventionally in order to gel dispersion liquid 2, the so-called resin of the oil absorption nature which absorbs and gels the hydrophobic medium which constitutes the dispersion liquid 2 concerned especially is suitably used as a gelling agent.

[0038] the bridging object of a low consistency of the polymer which made the oleophilic monomer the base unit as resin of this oil absorption nature although not limited to this -- or poly NORUBONENGOMU to which ring opening polymerization of NORUBONEN was carried out is raised. Although various approaches can be considered to gel the dispersion liquid 2 into which a porous layer 12 is infiltrated using the resin of the above-mentioned oil absorption nature Apply to the front face of a porous layer 12 the solution which contains the resin of oil absorption nature first, and after making it sink in into through-hole 12a of the porous layer 12 concerned, heating and drying and removing a solvent, dispersion liquid 2 are applied to the front face of the above-mentioned porous layer 12. Since the approach of making absorb dispersion liquid 2 and gelling in the resin of oil absorption nature with which it sank in into through-hole 12a is easy a process and can moreover be certainly filled up with gel in through-hole 12a, it is adopted suitably.

[0039] The oxygen permselective membrane which film-ized next the oxygen resolvent which dissolves the latter oxygen alternatively among two sorts of oxygen permselective membrane of this invention in the state of gel is explained. As an oxygen resolvent used by this invention, each various compound which dissolves oxygen alternatively as mentioned above is usable. As an example of this oxygen resolvent, although not limited to this, a perfluoro-butylamine etc. is raised.

[0040] A gelling agent is used in order to gel the above-mentioned oxygen resolvent. As a gelling agent, although each organic or inorganic conventionally well-known various ingredient is usable, especially absorptivity resin is used suitably. In order to film-ize the oxygen resolvent gelled with the above-mentioned gelling agent, various approaches can be considered, but while infiltrating a porosity supporting lamella and film-izing the gel concerned like the conventional liquid membrane raises an oxygen transmission rate, when maintaining membranous reinforcement, it is desirable.

[0041] As a porosity supporting lamella, what consists of a base film 11 and a porous layer 12 formed in the one side is suitably used so that it may be shown in having illustrated by previous oxygen permselective membrane, and the same thing, i.e., drawing 1. Although various approaches can be considered using the above-mentioned porosity supporting lamella 1 to film-ize gel of an oxygen resolvent Apply to the front face of a porous layer 12 the solution which contains the resin of absorptivity first, and make it sink in into through-hole 12a of the porous layer 12 concerned, and after heating and drying and removing a solvent, an oxygen resolvent is supplied to the front face of the above-mentioned porous layer 12. Since the approach of making absorb an oxygen resolvent and gelling in the resin of absorptivity with which it sank in into through-hole 12a is easy a process and can moreover be certainly filled up with gel in through-hole 12a, it is adopted suitably.

[0042] Although two sorts of oxygen permselective membrane [ each ] of this invention explained above can be used in various fields, such as an oxygen permeable membrane, it is especially used suitably as oxygen permselective membrane of a cell. Below, the cell of this invention which used the above-mentioned oxygen permselective membrane is explained. The configuration of this invention is applicable to various cells with the need of using oxygen permselective membrane.

While preparing the gas diffusion electrode which uses oxygen as an active material along with the above-mentioned air introduction hole in the cell container which has in more detail the air

introduction hole which leads to the open air, it is applicable to the cell of various methods which made oxygen permselective membrane intervene between this gas diffusion electrode and an air introduction hole. An air cell and a fuel cell are raised as this cell.

[0043] The cross section of one example of the air cell as a cell of this invention is shown in drawing 2. The cell B of drawing 2 carries out the laminating of the gas diffusion electrode 5, the diaphragm 6, and negative electrode 7 as the oxygen permselective membrane A, the \*\*\*\* water screen 4, and a positive electrode to order from a side-face [ in which the above-mentioned air introduction hole 31a was formed in the cell container 3 which prepared air introduction hole 31a which is well-informed about the open air in the one side face ] side. In addition, the above-mentioned air introduction hole 31a is formed, and the cell container 3 consists of a positive-electrode container 31 electrically connected with the gas diffusion electrode 5, and a negative electrode 7 and the negative-electrode container 32 connected electrically. It is sealed by the insulating gasket 8 between the above-mentioned positive-electrode container 31 and the negative-electrode container 32. Moreover, the diaphragm 6 has two-layer structure of the 1st and 2nd diaphragms 61 and 62.

[0044] As oxygen permselective membrane A, one side of two sorts of oxygen permselective membrane of this invention mentioned above is used among the above. This oxygen permselective membrane A is arranged, where it turned to the air introduction hole 31a side the porous layer 12 into which dispersion liquid 2 (or gel which made the oxygen solvent swell) were infiltrated and a base film 11 is turned to the \*\*\*\* water screen 4 side. The porous PTFE film same with having used it by the base film 11 as the \*\*\*\* water screen 4 etc. is used.

[0045] A gas diffusion electrode 5, a diaphragm 6, and a negative electrode 7 are constituted as usual. Moreover, as mentioned above, the electrolytic solutions, such as a potassium-hydroxide water solution, sink into a diaphragm 6. In addition, it is constituted as usual by the fuel cell.

[0046]

[Example] This invention is explained based on an example below.

0.3g of oxygen transporter which consists of an example 13-methoxy salcomine complex and 4-dimethylaminopyridine of equimolar was dissolved in one cc DMSO, the solution was produced, with 0.05g (a fatty-acid ethylene oxide addition product, HLB values 13.2-13.5) of nonionic surfactants, this solution was added to five cc perfluoropolyether, was written, was \*(ed), and dispersion liquid were produced.

[0047] As shown in drawing 1, after infiltrating these dispersion liquid 2 into the porous layer 12 (voidage of 40%, thickness of 10 micrometers) made from PTFE which has through-hole 12a of 0.22 micrometers of a majority of average apertures next, the oxygen permselective membrane A of an example 1 was laminating-manufactured by using this porous layer 12 as a base film 11. In addition, as a base film 11, addition reaction mold silicone rubber is applied to one side of a porous PTFE film (the average aperture of 0.1 micrometers, thickness of 50 micrometers), the hardening reaction was carried out, the thing in which the dispersion-liquid transparency prevention layer of 60 micrometers of thickness was formed was used, and the laminating of the porous layer 12 was carried out on this dispersion-liquid transparency prevention layer.

The oxygen permselective membrane A of an example 2 was manufactured like the example 1 except having set thickness of example 2 porous layer 12 to 110 micrometers.

having used it in the example 3 example 1 -- the same -- after having applied the solution of oil absorption nature resin [the trade name "OREOSOBUSL-130" by NIPPON SHOKUBAI Co., Ltd.] to the front face of the porous layer 12 with a thickness of 10 micrometers so that it might become the thickness of 5 micrometers by the bar coat method, and infiltrating through-hole 12a of a porous layer 12 into it, it was made to dry for 5 minutes at 100 degrees C

[0048] Subsequently, after having supplied the same dispersion liquid 2 as having used it for this porous layer 12 in the example 1, making the oil absorption nature resin with which it sank in into through-hole 12a absorb and gelling, the oxygen permselective membrane A of an example 3 was laminating-manufactured by using this porous layer 12 as the same base film 11 as having used it in the example 1.

having used it in the example 4 example 1 -- the same -- after having applied the solution of absorptivity resin [the trade name "AKUAYUKU" by Sumitomo Seika Chemicals Co., Ltd.] to the front face of the porous layer 12 with a thickness of 10 micrometers so that it might become the

thickness of 10 micrometers by the bar coat method, and infiltrating through-hole 12a of a porous layer 12 into it, it was made to dry for 15 minutes at 70 degrees C

[0049] Subsequently, this porous layer 12 was immersed for 5 minutes into the 20 cc perfluoro-butylamine which is an oxygen solvent, and after making the perfluoro-butylamine absorb in absorptivity resin and gelling it, the oxygen permselective membrane A of an example 4 was laminating-manufactured by using this porous layer 12 as the same base film 11 as having used it in the example 1. The cel for measurement is equipped with the oxygen permselective membrane A of each above-mentioned example, and they are the temperature of 25 degrees C, and the pressure of 1.2kg/cm<sup>2</sup> to the porous layer 12 side. When air was supplied, the gas chromatography analyzed the presentation of the gas penetrated to the base film 11 side of the oxygen permselective membrane A concerned.

[0050] And from the analysis result, the separation factor alpha (O<sub>2</sub>/CO<sub>2</sub>) of the oxygen to the separation factor alpha (O<sub>2</sub>/H<sub>2</sub>O) and carbon dioxide of oxygen to transmission rate [ of oxygen ] Q (O<sub>2</sub>) [cm<sup>3</sup> / cm<sup>2</sup>, and sec-cmHg] and a steam was computed. A result is shown in Table 1.

[0051]

[Table 1]

	Q (O <sub>2</sub> )	$\alpha$ (O <sub>2</sub> /H <sub>2</sub> O)	$\alpha$ (O <sub>2</sub> /CO <sub>2</sub> )
実施例 1	$5 \times 10^{-3}$	1.2	1.1
実施例 2	$20 \times 10^{-4}$	2.0	1.8
実施例 3	$8 \times 10^{-3}$	8	7
実施例 4	$7 \times 10^{-3}$	1.0	1.9

[0052] It included in the carbon button mold air cell (the diameter of 11.6mm, height of 5.4mm, R44 size) which shows the oxygen permselective membrane A manufactured in the example 5 example 1 to drawing 2 . And when the load of 15kohm was connected to the above-mentioned carbon button mold air cell under conditions of the temperature of 20 degrees C, and 70% of relative humidity and continuous discharge was performed, as a continuous line showed, compared with the case (a drawing destructive line shows) where the oxygen permselective membrane A is not incorporated, reinforcement was able to be carried out to drawing 3 about twice.

[0053]

[Effect of the Invention] As mentioned above, as explained in full detail, the oxygen permselective membrane of this invention can also prevent more certainly receipts and payments of a steam, and invasion of a carbon dioxide while it is excellent in the capacity to make oxygen penetrate alternatively. Therefore, many properties stabilize and are long lasting while the cell of this invention using the above-mentioned oxygen permselective membrane is excellent in the discharge engine performance, and it can be especially equal to prolonged use and storage.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing an example of the structure of the oxygen permselective membrane of this invention.

[Drawing 2] It is the sectional view using the above-mentioned oxygen permselective membrane showing an example of the structure of the cell of this invention.

[Drawing 3] It is the graph which shows the measurement result of the life of the cell manufactured in the example 5 of this invention.

[Description of Notations]

A Oxygen permselective membrane

1 Porosity Supporting Lamella

2 Dispersion Liquid

B Cell

3 Cell Container

31 Air Introduction Hole

5 Gas Diffusion Electrode

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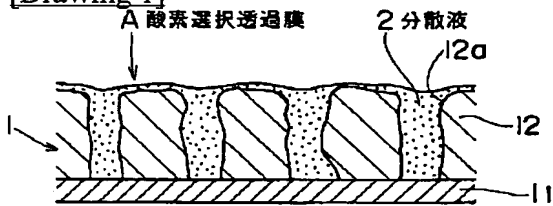
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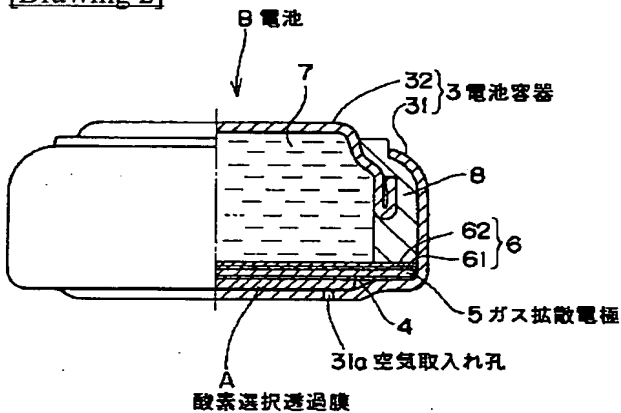
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## DRAWINGS

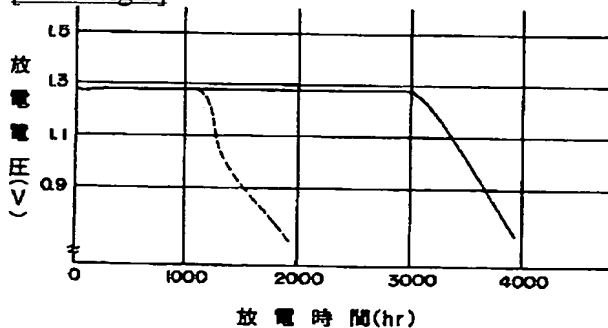
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]

# PATENT ABSTRACTS OF JAPAN

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(30)Priority

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Priority country : JP

## (54) OXYGEN PERMSELECTIVE FILM AND CELL USING THE FILM

(57)Abstract:

**PURPOSE:** To obtain an oxygen permselective film capable of preventing going out or in of water vapor and penetration of carbon dioxide by a method wherein a solution of an oxygen transporting carrier enveloping a metallic complex reversely bonded to oxygen is made into a film under a state wherein a dispersion liquid dispersed in an solute which is hydrophobic and slow in dissolving speed of carbon dioxide gels.

**CONSTITUTION:** In an oxygen permselective film A applied to an air cell or the like equipped with a gas dispersion electrode using oxygen as an active material, the film is made by impregnating a through hole 12a of a porous layer 12 of a porous support film 1 consisting of a basic film 11 and the porous layer 12 with a fluid dispersion 2. Then, after a dispersed oxygen transporting carrier solution adsorbs oxygen selectively in the fluid dispersion 2, oxygen is dispersed in the fluid dispersion 2 to detach or attach oxygen, and oxygen is made to permeate selectively the film. The fluid dispersion 2 is adjusted by dispersing the oxygen transporting carrier solution enveloping a metallic complex unusually reversibly bonded to oxygen into a solution which is hydrophobic and slow in dissolving speed of carbon dioxide, and a film is made in a gel state by a gelling agent swelled by the solute.



## LEGAL STATUS

[Date of request for examination]  
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[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]  
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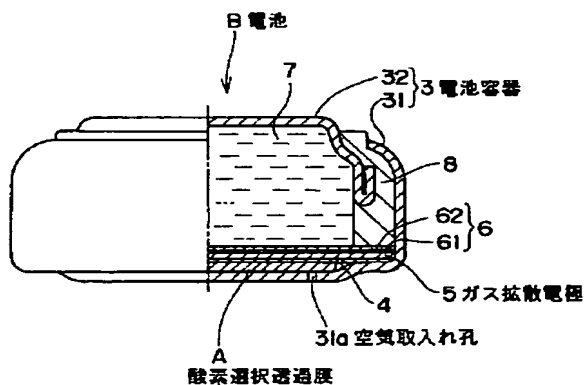
(74)代理人 弁理士 亀井 弘勝 (外1名)

(54)【発明の名称】 酸素選択透過膜およびそれを用いた電池

(57)【要約】

【構成】 酸素選択透過膜は、酸素輸送担体を、疎水性でかつ二酸化炭素の溶解速度の遅い媒質中に分散させた分散液、あるいは酸素溶解剤のゲルを膜化した。電池Bは、電池容器3の空気取り入れ孔31に沿って、酸素を活性物質とするガス拡散電極5を設け、このガス拡散電極5と空気取り入れ孔31との間に、上記酸素選択透過膜Aを介在させた。

【効果】 酸素選択透過膜は、酸素を選択的に透過させる能力にすぐれているとともに、水蒸気の出入りや二酸化炭素の侵入をより確実に防止できる。よって電池は、放電性能にすぐれるとともに諸特性が安定し、かつ長寿命であり、とくに長期間の使用や貯蔵に耐えうる。



## 【特許請求の範囲】

【請求項1】酸素と特異的かつ可逆的な結合をする金属錯体を含む酸素輸送担体の溶液を、疎水性でかつ二酸化炭素の溶解速度の遅い媒質中に分散させた分散液を、膜化したことを特徴とする酸素選択透過膜。

【請求項2】分散液を、媒質によって膨潤するゲル化剤によってゲル化した状態で膜化した請求項1記載の酸素選択透過膜。

【請求項3】酸素を選択的に溶解する酸素溶解剤を、ゲルの状態で膜化したことを特徴とする酸素選択透過膜。

【請求項4】酸素溶解剤を、吸水性樹脂によってゲル化した請求項3記載の酸素選択透過膜。

【請求項5】外気に通じる空気取り入れ孔を有する電池容器内に、上記空気取り入れ孔に沿って、酸素を活性物質とするガス拡散電極を設けるとともに、このガス拡散電極と空気取り入れ孔との間に、請求項1ないし4のいずれかに記載の酸素選択透過膜を介在させたことを特徴とする電池。

## 【発明の詳細な説明】

## 【0001】

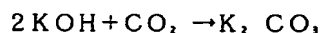
【産業上の利用分野】この発明は、酸素ガスを選択的に透過する機能を有する酸素選択透過膜と、それを用いた、空気電池、燃料電池等の電池に関するものである。

## 【0002】

【従来の技術と発明が解決しようとする課題】上記空気電池や燃料電池等の、酸素を活性物質に用いるガス拡散電極を備えた電池においては、電池容器に、外気に通じる空気取り入れ孔を設け、ここから取り入れた空気中の酸素を活性物質として使用することが一般に行われている。上記の電池は、実用に供せられる程度において、電池の内部抵抗、放電特性等の諸特性が安定しているが、より一層の安定性と長寿命化が望まれており、長寿命化への開発が続けられている。

【0003】たとえば従来の電池は、空気を取り入れ孔から水蒸気が出入りすることによる、電池内の電解液の濃度および体積の変動や、あるいは上記空気を取り入れ孔から侵入した二酸化炭素の吸収による、電解液の劣化等が生じるおそれがある。たとえば、濃度が30～35%程度の水酸化カリウム水溶液を電解液として用いた場合には、相対湿度が45～59%より高いと、この電解液が外部の湿気を取り込んで濃度低下と体積膨張を生じる結果、放電性能の低下や電解液の漏れ等を生じるおそれがあり、逆に相対湿度が上記範囲より低いと、電解液の蒸発がおこって、内部抵抗の増大や放電性能の低下等を生じるおそれがある。

【0004】また、上記水酸化カリウム水溶液が二酸化炭素を吸収すると、



の反応により電解液の変質がおこり、放電性能がえられなくなるため、電池の寿命が短くなる。この対策とし

て、電池容器の空気を取り入れ孔に、水蒸気を選択的に吸収する水蒸気選択吸収層を設けて水蒸気の透過速度を遅らせることが試みられたが、かかる水蒸気選択吸収層は、飽和状態に達すると水蒸気を吸収する能力が急速に失われてしまうという問題があった。またこの方法では二酸化炭素の侵入を防止できなかった。

【0005】漏液は、電池容器の空気取り入れ孔に紙や不織布等を配置することで、ある程度抑制できるが、これらのものには、水蒸気の出入りや二酸化炭素の侵入を防止する効果はなかった。空気取り入れ口を極端に小さくして、水蒸気の出入りや二酸化炭素の侵入を抑制することも検討されたが、この場合には酸素の供給量まで制限されるため、放電性能が犠牲になるという問題があった。また上記の方法では、水蒸気の出入りや二酸化炭素の侵入を完全に防止できないので、電池の諸特性が不安定化し、寿命が短くなるという問題の根本的な解決にはならなかった。しかもそれゆえに、体積膨張による漏液が生じると、空気取り入れ口が閉塞されて、放電性能がえられなくなるという問題もあった。

【0006】水蒸気の出入りや二酸化炭素の侵入を完全に防止しつつ、酸素を電池容器内に取り込むためには、酸素を、水蒸気や二酸化炭素より優先的に透過する膜が必要であった。しかし一般に、高分子等の有機材料のガス透過速度は、酸素の透過速度よりも水蒸気や二酸化炭素の透過速度の方が高い傾向にあるため、酸素を、水蒸気や二酸化炭素に比して優先的に透過させる膜の開発は容易でなかった。

【0007】血液に含まれるヘモグロビンは、酸素を結合する能力にすぐれている。たとえば1gのヘモグロビンは、37℃、大気圧の条件下で、1.34mlの酸素を結合する。しかも上記ヘモグロビンは、酸素分圧の高いところでは酸素をほぼ100%結合するが、分圧が低下して一旦、酸素が脱着しはじめると、急速に酸素を放出するという特性を有している。

【0008】そこで、上記ヘモグロビンを模した、酸素と特異的かつ可逆的な結合をする金属錯体を含む酸素輸送担体を使用することが検討された。酸素輸送担体を使用した酸素選択透過膜として代表的なものに、上記酸素輸送担体を適当な溶媒に溶解した溶液を、多孔質支持膜に含浸させて膜化した、いわゆる液体膜がある。

【0009】しかし上記液体膜においては、酸素輸送担体を良好に溶解しうる溶媒が、エチレングリコール等の親水性のものに限定されるとともに、上記溶液を良好に含浸させるために、多孔質支持膜に親水性が付与されるため、かかる液体膜は、水蒸気の出入りを防止する効果が不十分であるという問題があった。また上記親水性の有機溶媒は通常、二酸化炭素の溶解速度が速いため、当該液体膜は、二酸化炭素の侵入を防止する効果も不十分であった。

【0010】この発明の目的は、酸素を選択的に透過さ

せる能力にすぐれているとともに、水蒸気の出入りや二酸化炭素の侵入をより確実に防止できる酸素選択透過膜と、それを用いた、放電性能にすぐれるとともに諸特性が安定し、かつ長寿命の電池とを提供することにある。

【0011】

【課題を解決するための手段および作用】上記課題を解決するための、この発明の酸素選択透過膜は、酸素と特異的かつ可逆的な結合をする金属錯体を含む酸素輸送担体の溶液を、疎水性でかつ二酸化炭素の溶解速度の遅い媒質中に分散させた分散液を、膜化したことを特徴としている。

【0012】またこの発明の他の酸素選択透過膜は、酸素を選択的に溶解する酸素溶解剤を、ゲルの状態で膜化したことを特徴としている。さらにこの発明の電池は、外気に通じる空気取り入れ孔を有する電池容器内に、上記空気取り入れ孔に沿って、酸素を活性物質とするガス拡散電極を設けるとともに、このガス拡散電極と空気取り入れ孔との間に、上記2種の酸素選択透過膜のうちの一方を介在させたことを特徴としている。

【0013】上記構成からなる、この発明の酸素選択透過膜は、酸素輸送担体の溶液を、疎水性でかつ二酸化炭素の溶解速度の遅い媒質中に分散させた分散液を膜化したものゆえ、酸素を選択的に透過させる能力にすぐれているとともに、水蒸気の出入りや二酸化炭素の侵入をより確実に防止することもできる。また上記分散液を、多孔質支持膜に含浸させて膜化する際には、従来の、親水性の有機溶媒を使用した液体膜の場合のように、多孔質支持膜に親水性を付与する必要がないので、水蒸気の出入りを防止する効果が低下するおそれがないという利点もある。

【0014】さらに上記分散液を、媒質によって膨潤するゲル化剤によってゲル化した状態で膜化した場合には、当該ゲルが、多孔質支持膜の孔を塞ぐことになるので、水蒸気の出入りや二酸化炭素の侵入を防止する効果がより一層、向上する。また、この発明の他の酸素選択透過膜は、酸素を選択的に溶解する酸素溶解剤を、ゲルの状態で膜化してなるものであって、たとえばゲルを、従来の液体膜と同様に、多孔質支持膜に含浸させて膜化した場合に、当該ゲルが、多孔質支持膜の孔を塞ぐことになるので、水蒸気の出入りや二酸化炭素の侵入が確実に防止される。

【0015】また、上記ゲルを含浸させる多孔質支持膜は、従来のように親水性を付与する必要がないため、この点でも、水蒸気の出入りや二酸化炭素の侵入が確実に防止される。しかも、上記のように酸素溶解剤をゲル化したものは、たとえば夏の炎天下や熱帯地域等の気温の高い状況下で使用しても簡単に蒸発せず、長期に亘って膜を維持できる。

【0016】したがって、上記2種の酸素選択透過膜のうちの一方を用いたこの発明の電池は、放電性能にすぐ

れるとともに、水蒸気の出入りによる電解液の濃度および体積の変動や、二酸化炭素の吸収による電解液の劣化等がより確実に防止されるため、諸特性が安定し、かつ長寿命である。以下にこの発明を説明する。

【0017】まずこの発明の2種の酸素選択透過膜のうち前者の、酸素と特異的かつ可逆的な結合をする金属錯体を含む酸素輸送担体の溶液を、疎水性でかつ二酸化炭素の溶解速度の遅い媒質中に分散させた分散液を、膜化してなる酸素選択透過膜について説明する。酸素輸送担体を構成する金属錯体としては、上記のように、酸素と特異的かつ可逆的な結合をする機能を有する種々の金属錯体が、いずれも使用可能である。

【0018】かかる金属錯体の具体例としては、これに限定されないがたとえばシッフ塩基化合物；アミノ酸類；アミン系化合物；いおう、酸素、りん等の、窒素以外の元素を配位原子とする化合物の、コバルト、鉄、マンガ、パラジウム、ロジウム等の錯体等があげられる。中でもシッフ塩基化合物、とくにビス（サリチルアルデヒド）エチレンジイミンコバルト(II)類〔通称サルコミン類〕としての、3-メトキシサルコミン、5-メトキシサルコミン、3-メチルサルコミン等が好適に使用される。あるいはまたヒスチジンやアンモニアのコバルト錯体も好適に使用される。

【0019】上記金属錯体は、軸配位子と併用すると、酸素輸送担体としての機能がより一層向上する。かかる軸配位子としては、これに限定されないがたとえばイミダゾール、アミン、ピリジンなどがあげられる。金属錯体と軸配位子とは、等モルとなるように配合される。上記酸素輸送担体を溶解するための溶媒としては、酸素輸送担体を溶解しうる、種々の溶媒がいずれも使用可能である。かかる溶媒としては、これに限定されないがたとえば水；メタノール、エタノール、イソプロパノール等の低級アルコール類；エチレングリコール、ジエチレングリコール等の多価アルコール類；ジメチルスルホキシド（DMSO）、ジエチルホルムアミド（DEF）等の非プロトン性極性溶媒などの親水性の溶媒があげられる。

【0020】酸素輸送担体の溶液を分散させる媒質としては、疎水性でかつ二酸化炭素の溶解速度の遅い、種々の媒質が使用できる。かかる疎水性の媒質の具体例としては、これに限定されないがたとえば、ペルフルオルノルマルオクタン〔 $n-C_{18}F_{38}$ 、沸点 $104^{\circ}C$ 〕、ペルフルオルノルマルノナン〔 $n-C_{19}F_{40}$ 、沸点 $123^{\circ}C$ 〕、ペルフルオルトリブチルアミン〔 $(C_4F_9)_3N$ 、沸点 $177^{\circ}C$ 〕、ペルフルオロポリエーテル〔沸点 $300^{\circ}C$ 〕等の含フッ素化合物や、あるいはジメチルシロキサン等のシリコンオイルなどがあげられる。

【0021】なお疎水性の媒質としては、上記の中でもとくに、沸点の高いものがより好適に使用される。沸点の高い媒質は、たとえば夏の炎天下や熱帯地域等の気温

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の高い状況下で使用しても蒸発せず、長期に亘って膜を維持できるからである。この発明において、前記酸素輸送担体、溶媒および疎水性の媒質の配合量はとくに限定されないが、酸素輸送担体と溶媒は、溶媒1ccに対して酸素輸送担体を0.07ミリモル以上、配合するのが好ましい。

【0022】酸素輸送担体の配合量が上記範囲未満では、酸素を選択的に透過する機能が十分に発揮されないおそれがある。また、酸素輸送担体の溶媒への配合量の上限についてもとくに限定されないが、酸素透過速度を向上させるためには、酸素輸送担体の配合量は多ければ多いほど好ましく、電池の使用温度範囲において、酸素輸送担体が析出しない量まで配合することが可能である。この量は、酸素輸送担体と溶媒の種類によって異なり、たとえば後述する実施例1〜3で使用した、3-メトキシサルコミン錯体と4-ジメチルアミノピリジンとからなる酸素輸送担体とDMSOの場合は、30℃において、1ccのDMSOに対して酸素輸送担体を10ミリモルまで配合することが可能である。

【0023】なお酸素輸送担体の配合量は、酸素透過速度を向上させるためには、上記範囲内でもとくに0.5〜5ミリモルであるのが好ましい。酸素輸送担体を、上記の割合で溶媒に溶解した溶液は、疎水性の媒質5ccに対して、0.1〜4cc程度、とくに0.3〜2cc程度の割合で配合するのが好ましい。

【0024】疎水性の媒質5ccに対する酸素輸送担体の溶液の配合量が上記範囲未満では、酸素を選択的に透過する機能が十分に発揮されないおそれがある。逆に酸素輸送担体の溶液の配合量が上記範囲を超えた場合には、当該溶液を、疎水性の媒質中に均質に分散させるのが困難となり、溶液と媒質とが相分離して、酸素を効率的に輸送できなくなるおそれがある。

【0025】疎水性の媒質中に酸素輸送担体の溶液を分散させるためには、たとえば超音波振動、かく拌等の機械的手段、および界面活性剤の添加による化学的手段のうちのいずれか一方、あるいは両方が採用される。界面活性剤としては、イオン性、非イオン性の種々の界面活性剤が使用可能であるが、水蒸気の出入りを防止するために、できるだけ吸湿性の低いものが好ましく、たとえば非イオン性界面活性剤の場合はHLB値が15以下のものが好適に使用される。

【0026】HLB値が15以下である非イオン性界面活性剤の具体例としては、これに限定されないがたとえば、ソルビタン・トリオレエート（HLB値1.8）、ソルビタン・トリステアレート（HLB値2.1）、グリセリン・モノステアレート（HLB値3.8）、ソルビタン・モノオレエート（HLB値4.3）、ソルビタン・モノステアレート（HLB値4.7）、ソルビタン・モノパルミテート（HLB値6.7）等があげられる。

【0027】また、酸素輸送担体として銅あるいはコバルトの錯体を用いる場合に、アニオン性界面活性剤を使用すると、膜の酸素透過速度をより一層向上できる。これは、上記酸素輸送担体を溶解した溶液と、かかる溶液を分散した疎水性分散媒との界面に吸着したアニオン性界面活性剤のアニオンサイトが、溶液中の銅イオン、コバルトイオンを、静電的な相互作用によって上記界面に濃縮することで、当該界面における、酸素輸送担体による酸素の吸着反応の反応速度を増加させることが原因と考えられる。

【0028】界面活性剤の配合量についてはとくに限定されないが、疎水性の媒質1ccに対して、0.01〜0.1g程度であるのが好ましい。界面活性剤の配合量が上記範囲未満では、その添加効果が不十分となって、疎水性の媒質中に酸素輸送担体を十分に分散できないおそれがあり、逆に界面活性剤の配合量が上記範囲を超えた場合には、水蒸気が侵入しやすくなって、酸素の選択透過性が低下するおそれがある。

【0029】なお界面活性剤の配合量は、上記範囲内でもとくに0.03〜0.08gであるのが好ましい。上記各成分からなる分散液を膜化するには、従来の液体膜と同様に、分散液を、多孔質支持膜に含浸させて膜化すればよい。上記の構造の酸素選択透過膜の一例の断面を図1に示す。

【0030】図の酸素選択透過膜Aは、基膜11と、その片面に形成された多孔質層12とからなる多孔質支持膜1の、上記多孔質層12の通孔12aに、分散液2を含浸させて膜化したものである。上記酸素選択透過膜Aにおいては、分散液2中に分散された酸素輸送担体の溶液が、高酸素分圧である膜のガス供給側（図において上側）で酸素を選択的に吸着した後、分散液2中を拡散し、低酸素分圧である膜の透過側（図において下側）で酸素を脱着するという過程により、酸素が選択的に透過される。

【0031】上記酸素選択透過膜Aのうち、多孔質支持膜1を構成する基膜11としては、酸素の透過性にすぐれ、しかも分散液2や電池の電解液、あるいは水蒸気等を通過しないものが好適に使用される。かかる基膜11としては、これに限定されないがたとえば、多孔性のポリテトラフルオロエチレン（PTFE）膜等の、それ自体は水性で、かつごく細かな通孔を有し酸素の透過性にすぐれたフィルムの片面に、シリコンゴム等の、やはり酸素の透過性がよく、しかも分散液を構成する疎水性の媒質に溶けない材質からなる分散液透過防止層を積層したものがあげられる。

【0032】上記2層構造の基膜11においては水性のフィルムは、電解液の漏液や、あるいは水蒸気の通過を防止するために機能し、分散液透過防止層は、分散液2の通過を防止するために機能する。また、上記基膜11の片面（好ましくは分散液透過防止層が形成された側

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の面)に形成される多孔質層12としては、多数の通孔12aを有する、PTFE等のはっ水性の材料からなる膜が好適に使用される。

【0033】かかる多孔質層12の厚みは、図1から明らかなように、分散液2の膜(液体膜)の厚みに相当し、液体膜の厚みは、酸素選択透過膜Aにおける酸素を選択的に透過し、かつ水蒸気の出入りや、二酸化炭素の侵入を防止する機能を決定する上で重要な要素であるので、酸素選択透過膜Aに求められる上記の各特性に応じ、最適な範囲を設定すればよく、具体的な厚みの範囲はとくに限定されない。

【0034】しかし上記多孔質層12の厚みは、一般的には、5~200 $\mu$ mの範囲内であるのが好ましい。多孔質層12の厚みが上記範囲未満では、当該多孔質層12に保持される分散液の量が少なくなって、酸素を選択的に透過し、かつ水蒸気の出入りや二酸化炭素の侵入を防止する能力が低下するおそれが生じ、逆に上記範囲を超えた場合には、通孔12aの距離が長くなって、酸素を透過する能力が低下するおそれが生じる。なお多孔質層12の厚みは、上記範囲内でもとくに1.5~10 $\mu$ mであるのが好ましい。

【0035】また、上記多孔質層12における、通孔12aの孔径や、多孔質層12の全体の空隙率等についてもとくに限定されないが、通孔12aの孔径は、平均孔径であらわして0.01~10 $\mu$ m程度が好ましく、多孔質層12の空隙率は、20~90%程度が好ましい。通孔12aの平均孔径が上記範囲未満では、多孔質層12の厚みにもよるが、酸素選択透過膜Aにおける、酸素を透過する能力が低下するおそれが生じる。また逆に、通孔12aの平均孔径が上記範囲を超えた場合には、分散液2の表面張力によって、当該通孔12aが分散液2を保持する能力が低下して、図1に示すような液体膜を形成できなくなり、そのために、水蒸気の出入りや二酸化炭素の侵入を防止できなくなるおそれが生じる。なお通孔12aの平均孔径は、上記範囲内でもとくに0.1~5 $\mu$ mであるのが好ましい。

【0036】一方、多孔質層12の空隙率が前記範囲未満では、当該多孔質層12中に含浸できる分散液の量が少なくなって、酸素を選択的に透過し、かつ水蒸気の出入りや二酸化炭素の侵入を防止する能力が低下するおそれが生じ、逆に前記範囲を超えた場合には、多孔質層12の強度が不十分になるおそれがある。なお多孔質層12の空隙率は、上記範囲内でもとくに40~80%程度が好ましい。

【0037】上記多孔質層12に含浸させる分散液2をゲル化した場合には、前述したようにゲルが、多孔質層12の孔を塞ぐことになるので、酸素選択透過膜Aにおける、水蒸気の出入りや二酸化炭素の侵入を防止する効果がより一層、向上する。分散液2をゲル化するには、従来公知の種々のゲル化剤がいずれも使用できるが、と

くに、当該分散液2を構成する疎水性の媒質を吸収してゲル化する、いわゆる吸油性の樹脂が、ゲル化剤として好適に使用される。

【0038】かかる吸油性の樹脂としては、これに限定されないがたとえば、親油性のモノマーを基本単位とした重合体の、低密度の橋かけ体や、あるいはノルボネンを開環重合させたポリノルボネンゴム等があげられる。上記吸油性の樹脂を用いて、多孔質層12に含浸させる分散液2をゲル化するには種々の方法が考えられるが、まず吸油性の樹脂を含む溶液を多孔質層12の表面に塗布して、当該多孔質層12の通孔12a内に含浸させ、加熱、乾燥して溶媒を除去した後、上記多孔質層12の表面に分散液2を塗布して、通孔12a内に含浸された吸油性の樹脂中に分散液2を吸収させてゲル化する方法が、工程が簡単で、しかもゲルを通孔12a内に確実に充填できるため、好適に採用される。

【0039】つぎに、この発明の2種の酸素選択透過膜のうち後者の、酸素を選択的に溶解する酸素溶解剤を、ゲルの状態で膜化した酸素選択透過膜について説明する。この発明で使用する酸素溶解剤としては、上記のように酸素を選択的に溶解する種々の化合物が、いずれも使用可能である。かかる酸素溶解剤の具体例としては、これに限定されないがたとえばペルフルオロブチルアミン等があげられる。

【0040】上記酸素溶解剤をゲル化するためにはゲル化剤が使用される。ゲル化剤としては、有機または無機の従来公知の種々の材料が、いずれも使用可能であるが、とくに吸水性樹脂が好適に使用される。上記ゲル化剤によってゲル化した酸素溶解剤を膜化するには、種々の方法が考えられるが、従来の液体膜と同様に、当該ゲルを、多孔質支持膜に含浸させて膜化するのが、酸素透過速度を向上させるとともに、膜の強度を維持する上で好ましい。

【0041】多孔質支持膜としては、先の酸素選択透過膜で例示したのと同様のもの、すなわち図1に示すように基膜11と、その片面に形成された多孔質層12とからなるものが好適に使用される。上記多孔質支持膜1を用いて、酸素溶解剤のゲルを膜化するには種々の方法が考えられるが、まず吸水性の樹脂を含む溶液を多孔質層12の表面に塗布して、当該多孔質層12の通孔12a内に含浸させ、加熱、乾燥して溶媒を除去した後、上記多孔質層12の表面に酸素溶解剤を供給して、通孔12a内に含浸された吸水性の樹脂中に酸素溶解剤を吸収させてゲル化する方法が、工程が簡単で、しかもゲルを通孔12a内に確実に充填できるため、好適に採用される。

【0042】以上で説明した、この発明の2種の酸素選択透過膜はいずれも、酸素富化膜等の種々の分野で使用できるが、とくに電池の酸素選択透過膜として、好適に使用される。つぎに、上記酸素選択透過膜を用いた、こ

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の発明の電池について説明する。この発明の構成は、酸素選択透過膜を使用する必要がある種々の電池に適用することができる。より詳しくは、外気に通じる空気取り入れ孔を有する電池容器内に、上記空気取り入れ孔に沿って、酸素を活性物質とするガス拡散電極を設けるとともに、このガス拡散電極と空気取り入れ孔との間に酸素選択透過膜を介在させた、種々の方式の電池に適用可能である。かかる電池としては、空気電池、燃料電池があげられる。

【0043】この発明の電池としての空気電池の、一実施例の断面を図2に示す。図2の電池Bは、その一側面に外気に通じる空気取り入れ孔31aを設けた電池容器3内に、上記空気取り入れ孔31aが形成された側面側から順に、酸素選択透過膜A、はっ水膜4、正極としてのガス拡散電極5、隔膜6および負極7を積層したものである。なお電池容器3は、上記空気取り入れ孔31aが形成され、ガス拡散電極5と電気的に接続された正極容器31と、負極7と電気的に接続された負極容器32とで構成されている。上記正極容器31と負極容器32との間は、絶縁ガasket 8によって密封されている。また隔膜6は第1および第2の隔膜61、62の2層構造になっている。

【0044】上記のうち酸素選択透過膜Aとしては、前述したこの発明の2種の酸素選択透過膜のうち的一方が使用される。かかる酸素選択透過膜Aは、分散液2（または酸素溶解剤を膨潤させたゲル）を含浸させた多孔質層12を空気取り入れ孔31a側、基膜11をはっ水膜4側に向けた状態で配置される。はっ水膜4としては、基膜11で使用したのと同様の、多孔性のPTFE膜等が使用される。

【0045】ガス拡散電極5、隔膜6および負極7は、従来同様に構成される。また隔膜6には前述したように、水酸化カリウム水溶液等の電解液が含浸される。なお燃料電池についても、従来同様に構成される。

【0046】

【実施例】以下にこの発明を、実施例に基づいて説明する。

#### 実施例1

3-メトキシサルコミン錯体と、等モルの4-ジメチルアミノピリジンとからなる酸素輸送担体0.3gを、100ccのDMSOに溶解して溶液を作製し、この溶液を、非イオン性界面活性剤（脂肪酸エチレンオキシド付加物、HLB値13.2~13.5）0.05gとともに、5ccのペルフルオロポリエーテルに加えてかく拌して、分散液を作製した。

【0047】つぎにこの分散液2を、図1に示すように、平均孔径0.22μmの多数の通孔12aを有するPTFE製の多孔質層12（空隙率40%、厚み10μ

m）に含浸させた後、この多孔質層12を基膜11と積層して、実施例1の酸素選択透過膜Aを製造した。なお基膜11としては、多孔性のPTFEフィルム（平均孔径0.1μm、厚み50μm）の片面に付加反応型シリコーンゴムを塗布し、硬化反応させて、膜厚60μmの分散液透過防止層を形成したものを使用し、この分散液透過防止層の上に、多孔質層12を積層した。

#### 実施例2

多孔質層12の厚みを110μmとしたこと以外は、実施例1と同様にして、実施例2の酸素選択透過膜Aを製造した。

#### 実施例3

実施例1で使用したのと同じ、厚み10μmの多孔質層12の表面に、吸油性樹脂〔日本触媒（株）製の商品名「オレオソープSL-130」〕の溶液を、バーコート法にて、厚み5μmとなるように塗布して、多孔質層12の通孔12aに含浸させた後、100℃で5分間、乾燥させた。

【0048】ついでこの多孔質層12に、実施例1で使用したのと同じ分散液2を供給し、通孔12a内に含浸された吸油性樹脂に吸収させてゲル化した後、この多孔質層12を、実施例1で使用したのと同じ基膜11と積層して、実施例3の酸素選択透過膜Aを製造した。

#### 実施例4

実施例1で使用したのと同じ、厚み10μmの多孔質層12の表面に、吸水性樹脂〔住友精化（株）製の商品名「アクアユーク」〕の溶液を、バーコート法にて、厚み10μmとなるように塗布して、多孔質層12の通孔12aに含浸させた後、70℃で15分間、乾燥させた。

【0049】ついでこの多孔質層12を、酸素溶解剤である20ccのペルフルオロブチルアミン中に5分間、浸漬して、ペルフルオロブチルアミンを吸水性樹脂中に吸収させてゲル化した後、この多孔質層12を、実施例1で使用したのと同じ基膜11と積層して、実施例4の酸素選択透過膜Aを製造した。上記各実施例の酸素選択透過膜Aを測定用のセルに装着し、その多孔質層12側に、温度25℃、圧力1.2kg/cm<sup>2</sup>の空気を供給した際に、当該酸素選択透過膜Aの基膜11側に透過してきたガスの組成を、ガスクロマトグラフィーで分析した。

【0050】そして分析結果から、酸素の透過速度Q(O<sub>2</sub>)〔cm<sup>3</sup>/cm<sup>2</sup>・sec・cmHg〕、水蒸気に対する酸素の分離係数α(O<sub>2</sub>/H<sub>2</sub>O)、および二酸化炭素に対する酸素の分離係数α(O<sub>2</sub>/CO<sub>2</sub>)を算出した。結果を表1に示す。

【0051】

【表1】

	$Q(O_2)$	$\alpha(O_2/H_2O)$	$\alpha(O_2/CO_2)$
実施例 1	$5 \times 10^{-3}$	12	11
実施例 2	$20 \times 10^{-4}$	20	18
実施例 3	$8 \times 10^{-3}$	8	7
実施例 4	$7 \times 10^{-3}$	10	19

## 【0052】実施例5

実施例1で製造した酸素選択透過膜Aを、図2に示すボタン型空気電池（直径11.6mm、高さ5.4mm、R44サイズ）に組み込んだ。そして上記ボタン型空気電池に、温度20℃、相対湿度70%の条件下で15kΩの負荷を接続して連続放電を行ったところ、図3に実線で示すように、酸素選択透過膜Aを組み込まない場合（図中破線で示す）に比べて、2倍近く長寿命化することができた。

## 【0053】

【発明の効果】以上、詳述したようにこの発明の酸素選択透過膜は、酸素を選択的に透過させる能力にすぐれているとともに、水蒸気の出入りや二酸化炭素の侵入をより確実に防止することも可能である。したがって、上記酸素選択透過膜を用いたこの発明の電池は、放電性能にすぐれるとともに諸特性が安定し、かつ長寿命であり、\*

10\*とくに長期間の使用や貯蔵に耐えうるものである。

## 【図面の簡単な説明】

【図1】この発明の酸素選択透過膜の構造の一例を示す断面図である。

【図2】上記酸素選択透過膜を用いた、この発明の電池の構造の一例を示す断面図である。

【図3】この発明の、実施例5で製造した電池の寿命の測定結果を示すグラフである。

## 【符号の説明】

A 酸素選択透過膜

1 多孔質支持膜

2 分散液

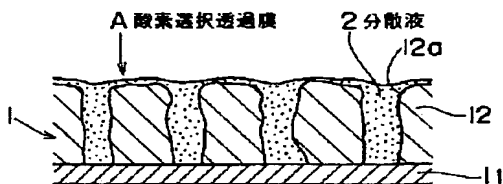
B 電池

3 電池容器

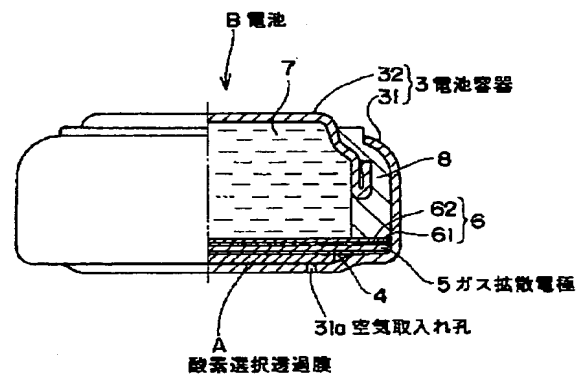
31 空気取り入れ孔

5 ガス拡散電極

【図1】



【図2】



【図3】

